Glycerol and Catalysis by Waste/Low-Cost Materials—A Review

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Abstract: The growing global demand for renewable energy sources can be reached using biofuels such as biodiesel, for example. The most used route to produce biodiesel is the transesterification reaction of oils or fats with short-chain alcohols, generating fatty acid esters (biodiesel) and a very important by-product, glycerol (Gly). Gly is widely used in different sectors of the industry, and in order to add value to this by-product, heterogeneous catalysis becomes a relevant tool, whether to transform glycerol into other chemical products of interest or even use it in the production of catalysts. Among the several studies found in the literature, the use of low-cost materials and/or wastes from the most diverse activities to prepare active catalytic materials for the transformation of Gly has been increasingly reported due to its valuable advantages, especially related to the cost of raw materials and environmental aspects. Thus, this brief review article presents the relationship between catalysis, low-cost materials, waste, and glycerol, through different studies that show glycerol being transformed through reactions catalyzed by materials produced from low-cost sources/waste or with the glycerol itself used as a catalyst.

Keywords: glycerol; catalysis; low-cost materials; waste valorization

1. Introduction

Regarding the concept of sustainability, an extremely important issue that needs to be addressed is global warming and climate change caused by anthropogenic greenhouse gas emissions. Such a situation generates a necessity to make a transition from fossil fuels to renewable energy, such as biofuels and low-emission or carbon-free energy [1].

Over the last decades, biodiesel production has grown due to the conventional process of transesterification of edible, inedible, and residual vegetable oils to replace fossil fuels [2,3]. Biodiesel is a mixture of methyl or ethyl esters produced by transesterification (Figure 1) of triglycerides (1), which are long-chain carboxylic acids (C_8–C_{24}) (3) linked to a molecule of glycerol or glycerin ($C_3H_8O_3$) (4) [1,4].
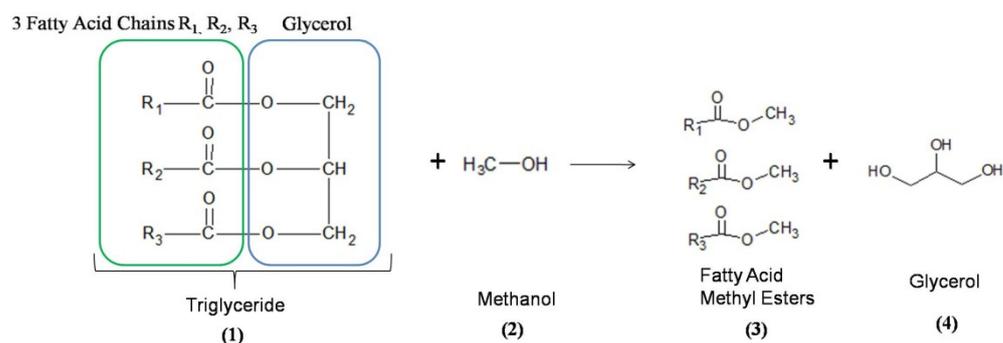
Figure 1. Production of glycerol from the transesterification of adapted triglycerides [2].

Recent prospects for the biodiesel market according to the database compiled by the Organization for Economic Co-operation and Development (OECD) and the Food and Agriculture Organization (FAO) [5] can be seen in Figure 2. Crude Glycerol is the main by-product (at 10% by weight) of biodiesel production [6]. In 2021, the global production of crude glycerol was close to 5 billion liters, expected to increase by 3% per year between 2021 and 2030 [2,5,7]. The recent update of the OECD/FAO report [5] shows that the prospects for this decade indicate that world consumption of biodiesel continues to grow, even at a slower pace.
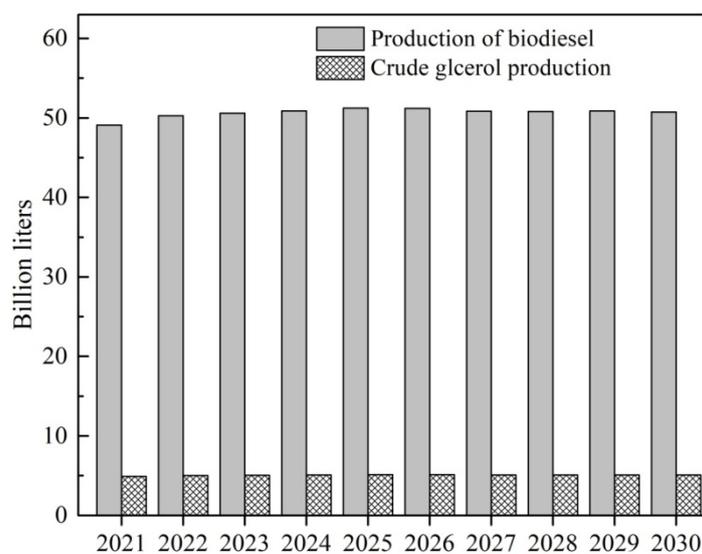

Figure 2. World biodiesel market projections. Adapted from [5].

Glycerol, propane-1,2,3-triol, is a symmetrical polyol with three hydroxyl groups (OH) with different reactivity [8]. By distillation, crude glycerol can be purified and becomes glycerin (technical grade), which can be used as a reagent in different industries, including the food, cosmetic, and pharmaceutical industry and in the production of various chemical products such as lactic acid, acrolein, citric acid, 1,3-propanediol, anti-freezing products, and others [2,3,7,9]. However, the estimated demand for commercial use still does not exceed 20% of this total; this demonstrates the importance of its valorization [1,2,7,9]. Furthermore, the use of residual glycerol meets a sustainability trend in the chemical industry that uses raw glycerol residues to obtain value-added products. With the advance of the biorefinery concept, glycerol has become a platform chemical and not just a final product with infinite applications [10]. Figure 3 shows some value-added chemicals that can be obtained from several chemical transformations through the conversion of glycerol (21), with applications in the polymer, agrochemical, and pharmaceutical industries [11].
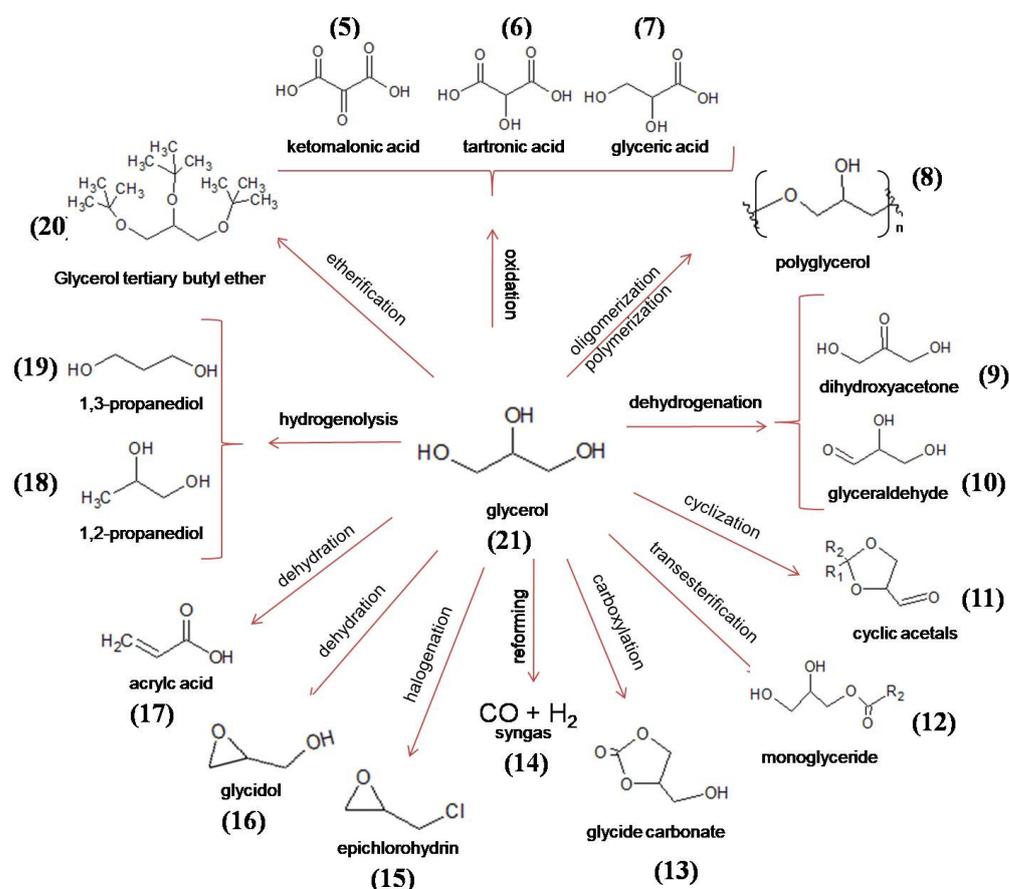
Figure 3. Routes for transforming glycerol into various value-added chemicals.

New processes or routes and products are being investigated for this polyol, while eco-friendly catalysts are created with a focus on their simplicity while also looking for greater selectivity and activity [1,2,7,10,12].

To improve the sustainability of the process in particular, the search for cheaper and environmentally friendly raw materials for catalyst production, such as wastes, has been the focus of research groups around the world. Therefore, this review covers recent advances in the catalytic reactions of Gly, more specifically in the last 15 years, with special attention to the heterogeneous catalysis based on catalysts from low-cost/waste materials applied in the recovery of residual Gly from biofuel production.

2. Glycerol Conversion Processes

Different catalytic processes can be used in the conversion of glycerol (Figure 3). This versatility is due to the presence of hydroxyl groups. Therefore, Gly is considered in the biorefinery as a chemical platform, since each process to which the molecule is subjected results in different products [13,14].

Numerous major Gly transformation pathways have been reported in the literature involving hydrogenolysis [15], etherification [16], esterification [17], acetalization [18], ketalization [10], and others [2,3,7]. Each reaction can be catalyzed by green catalysts derived from different waste sources, such as palm kernel shell [19], carbonaceous [20], eggshell [21], peanut shell [22], and Gly itself [23].

2.1. Clay

Clay is an abundant material and can be obtained from the environment at no cost. Recently, Zahid et al. [24] and Amri et al. [10] prepared a catalyst based on crude kaolin clay and smectite from Tunisian clay, calcined and activated with an acid activation technique

with hydrochloric acid (HCl, 3 mol L^{-1}), and later evaluated its catalytic properties in the reaction of Gly and acetone during ketalization, and the maximum yield of solketal obtained was 84% and 71%, respectively.

The ketalization reaction has gained potential interest in applications for the better use of excess glycerol produced from the biodiesel process [24]. Gly can be used for the synthesis of biodiesel additives, e.g., solketal, which improves cold properties and reduces the viscosity of the biodiesel formulation. It is well known that heterogeneous acid systems used as catalysts for this reaction lead to the formation of five-membered solketal [2,2-dimethyl-1,3-dioxane-4-methanol, (24)] and six-membered acetal [2, 2-dimethyl-dioxane-5-ol, (25)] members (Figure 4). In general, their solketal yields depend on the surface acidity of the catalyst.
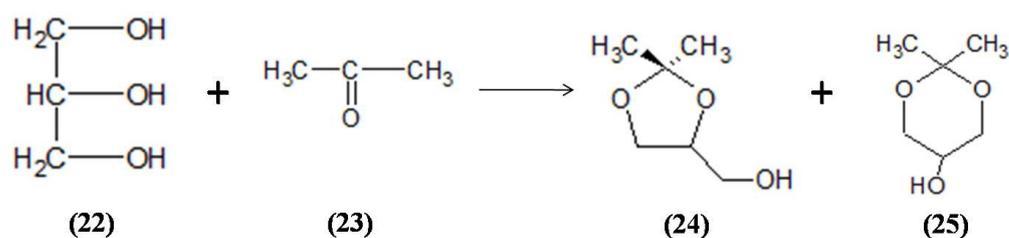

Figure 4. Main reaction products in the acetalization of glycerol (I) with acetone. Adapted from [12].

Within this context, some low-cost heterogeneous catalysts have been applied in these processes for Gly recovery, and investigations have proven that the catalytic properties of acid-modified clays can be adjusted by varying the acid concentration used for clay modification [12]. The effect of acid activation of natural montmorillonite with nitric acid (HNO$_3$, 0.5 mol L^{-1}) on the physicochemical and catalytic properties of solids in the acetylation of glycerol was investigated by Timofeeva et al. [12]. The catalyst with Brønsted acidity was more active (54% conversion of Gly, selectivity of 97.7% in solketal, with acetone/glycerol molar ratio of 2.5/1) and stable for at least 3 catalytic cycles under solvent free at an acetone/glycerol molar ratio of 4.1/1 and 50 °C.

Recently, in 2022, Wang et al. [25] explored a Co/SEP-NaOH catalyst manufactured with a complete activation of natural sepiolite (SEP) by NaOH that exhibited a well-developed hierarchical porous structure and highly improved catalytic behavior in the steam reforming of Gly. The Co/SEP-NaOH catalyst showed the highest conversion (92%) and H$_2$ yield (68%); in addition, the H$_2$ yield and conversion remained relatively stable in the period from 50 to 600 °C.

In 2017, for the first time, Menor et al. [26] reported a comparative study between catalysts based on natural sepiolite with Ni incorporated by two different methods: prepared by precipitation and impregnation of incipient moisture. The catalyst showed improved catalytic properties at low-to-moderate reaction temperatures (350–500 °C): higher catalytic activity (100% Gly conversion at 500 °C), 53% H$_2$ selectivity, and less unwanted products (CO, CH$_4$, C$_3$H$_6$O, C$_3$H$_6$ and C$_2$H$_4$). This study demonstrates that the Ni incorporation method significantly affects the size of metallic nickel particles and their interaction with the sepiolite support. The precipitation method allowed for preparing a material with Ni with greater activity and selectivity at low temperatures and greater resistance to the oxidation of metallic nickel and coke deposition.

In addition, some authors report the use of different types of calcium oxide (CaO) catalysts derived from natural materials. Algoufi et al. [27] synthesized glycerol carbonate (GC) from glycerol using CaO–MgO mixed oxide catalysts prepared from natural dolomite. Transesterification of glycerol with dimethyl carbonate in calcined dolomite results in a maximum yield of 94% glycerol carbonate with a maximum conversion of 97% glycerol. The catalyst provided 84% glycerol conversion and 79% glycerol carbonate yield during the fourth reaction cycle. On the other hand, when the catalyst is recalcined at 800 °C after

recovery for reuse in the next reaction cycle, the catalyst assumes activity equivalent to that of the fresh catalyst.

Based on the above results, for the first time, Azri et al. [28] reported the preparation of a solid Cu/dolomite acid catalyst by the impregnation technique, using mineral dolomite as a support for 10, 20, and 30% by weight of Cu. Of the catalysts investigated in the reported protocol, 20%Cu/Dol provided maximum glycerol conversion (100%), with a selectivity of 92.21% for 1,2-PDO. The results of the regeneration study after five reaction cycles indicated that 20%Cu/Dol maintained high values (95%) of glycerol conversion and selectivity (84%) of the recovered 1,2-PDO, suggesting that the spent catalyst was free of coke. Interestingly, the reaction pressure (2 MPa) was lower than that required in the hydrogenolysis of glycerol using hydrogen gas, while the same group reported similar results for a higher pressurized protocol (200 °C, 4 MPa, and 10 h heating time) reaction [29], making a comparative study between Cu/Dol and (Ni/Dol, Co/Dol, Fe/Dol, Zn/Dol) for the same reaction. The Cu/Dol catalyst showed promising activity when compared to other catalysts with a higher glycerol conversion and a 1,2-PDO selectivity of (78.5%) and (79%). The discovery of these studies is a valuable step in the search for catalysts free of expensive metals and that are more environmentally benign for the development of biomass valorization.

2.2. Fly Ash

Fly ash is obtained by burning charcoal of vegetable origin, and several heterogeneous catalysts of high catalytic activity were developed, including alkali metal oxide or mixed metal oxide, alkali phosphate, alkali silicate, and ionic liquid. However, they presented some problems, such as high setup costs or complex setup procedures. In this context, the development of low-cost, high-activity basic catalysts has become an important aspect in the field of transesterification of glycerol with dimethyl carbonate [30].

Algoufi and Hameed [30] synthesized K-zeolite derived from coal fly ash by hydrothermal treatment (160 °C for 8 h) and activated it in an oven at a temperature of 450 °C for 4 h. The K-zeolite catalyst showed that the Gly conversion and glycerol carbonate yield of the process were 100% and 96%, respectively. K-zeolite showed good stability, with about 6% reduction in Gly conversion (94%) and glycerol carbonate yield (90%) during recycling experiments, and was sustained for four consecutive runs.

The efficiency of zeolites was also proven in the study by Khanday et al. [31], who synthesized zeolite from mesoporous palm ash (OPAZ) and impregnated it with various charges of lithium ions, resulting in the catalyst being applied in the transesterification reaction under ideal reaction conditions (70 °C, 90 min, molar ratio DMC/Gly of 2 and 2% by weight of catalyst charge) in the conversion of Gly, and showing a high conversion (100%) and yield via glycerol carbonate (98.1%). The high efficiency can be explained by the basic character of the catalyst (Li-OPAZ), which occurred by lithium impregnation, explaining the high catalytic activity.

Recently, Arora et al. [32] used a catalyst based on 2% lithium (Li) by weight impregnated with coal fly ash (CFA) and calcined at 500 °C, which showed maximum conversion and yield of glycerol (96.33) and glycerol carbonate (91.74%), respectively, at 90 °C, with a reaction time of 2 h. Furthermore, the kinetics of the transesterification reaction had a calculated activation energy of 26.50 kJ·mol^{-1}. Lithium was also used by Pradhan et al. [33] in a sustainable approach to reusing abundantly produced industrial waste 'pond ash (PA)', and synthesis using a series of low-cost catalysts doped with active metals lithium (Li), potassium (K), and barium (Ba) was performed by the simple wet impregnation method. Barium showed better results and with the decrease in Ba content from 18.3% to 9.7% on the catalyst surfaces, and conversion and selectivity also decreased from 98% to 93% of Gly and from 94% to 92% of glycerol carbonate.

In another work, Indran et al. [34] proposed for the first time the use of waste material, specifically boiler ash (BA), as a catalyst for the synthesis of glycerol carbonate from glycerol and urea. The BA 900 catalyst was prepared by calcination at 900 °C for 4 h, with an average

percentage of catalytic activity of 93.6 ± 0.4% Gly conversion, 90.1 ± 1.0% GC selectivity, and 84.3 ± 1.1% GC glycerol carbonate yield, respectively, and also showing a promising approach for glycerol carbonate synthesis using residual BA.

Another study involving palm oil ash (OPFA) as a catalyst was developed by Okoye et al. [35], in which they optimized the conversion of Gly to produce GC glycerol carbonate. Delesma et al. [36] studied the kinetics and mechanisms of esterification of Gly using the OPFA catalyst cited above [35] at the theoretical density functional (DFT) level to categorize the most likely pathways to achieve a high conversion of Gly, highlighting the reaction steps. The cyclization reaction is thermodynamically more favorable with a Gibbs free energy of -310 kcal mol^{-1}, suggesting a viable exothermic reaction in the spontaneous formation of the GC and that the presence of the catalyst is crucial to allow such a reaction to occur.

Recently, Gao et al. [37] produced two works in which they investigated the catalytic behavior of Ni-based catalysts supported by coal fly ash prepared by the wet impregnation method for application in catalytic steam reforming. The catalytic performance of yNi-FAx catalysts in catalytic steam reforming (GSR) was investigated. According to their results, the addition of 7.5% by weight of Ni to FA showed better performance in terms of activity (conversion of Gly to gaseous products = 98%, H$_2$ yield = 78.8%) and remained stable for 40 h in operation. In the second work [38], they improved the physicochemical properties of the catalyst. The sequence of treatments considerably affects the characteristics of the developed catalyst, improving performance, conversion of Gly into gas (99.2%), and H$_2$ yield (74.5%).

2.3. Urban Waste

Urban waste represents a major environmental problem and transforming it into biochar for application as catalysts can be a sustainable alternative. Biochars are efficient and low-cost catalytic materials for transesterification reactions due to their texture characteristics and relatively high surface area. Based on this precept, Shikhaliyev et al. [39] worked with carbonized fishmeal at various temperatures (550−750 °C). Biochar carbonized at 650 °C was more suitable for use in transesterification to achieve 99.5% glycerol carbonate (GC) yield and complete glycerol conversion. The addition of solvent (methanol) sustains five cycles of reuse with a GC yield greater than 92%.

In this context, a pioneering work by Wang et al. [40] used disposable diaper waste (DBDW) made of non-biodegradable superabsorbent polymer (SAP), i.e., sodium polyacrylate, which has been an increasingly serious environmental problem. In this study, SAP in DBDW was carbonized at different temperatures (200 °C to 600 °C for 30 min) to prepare a series of basic catalysts. The catalytic capacity of these catalysts in the transesterification reaction of glycerol (75 °C for 1 h) with dimethyl carbonate (DM) was compared. Among them, the catalyst showed good catalytic activity with 95.6% glycerol conversion and 93.6% glycerol carbonate yield. In addition, it exhibited high reuse after eight reuses in the reaction: 91.8% (Gly) and 90.1% (GC).

The development of low-cost, high-activity basic catalysts has become an important aspect in the field of glycerol valorization [28]. Roschat et al. [41] showed the feasibility of applying CaO catalysts derived from natural sources (calcined at 800 °C for 3 h) to provide a glycerol carbonate yield greater than 92.1%. The use of natural materials, formed by calcium carbonate, has recently become an interesting approach for the development of cheap and widely available basic catalysts. The work of Barros et al. [21] evaluated the use of calcined eggshell residues (at 900 °C for 2 h) as a catalytic precursor in the etherification reaction of Gly in the absence of solvent to obtain glycerol oligomers. The catalyst provided 85% glycerol conversion and 43% oligomer (Di- and Triglycerol) yield. The catalytic study also indicated that the long-term reaction does not occur satisfactorily at 200 °C and higher temperatures (245 °C), as they lead to higher polymer chains and unwanted acrolein, in addition to the low stability caused by leaching in the medium reaction.

2.4. Industrial Waste

An attractive area of research that has recently emerged in the field of developing affordable and efficient catalysts for numerous catalytic reactions has been the exploration of industrial solid waste and other cheap and abundant materials containing alkali, alkaline earth, and transition metals (e.g., magnesium, iron, oxides of silicon, titanium, or aluminum), due to their supporting properties and promoting effects. Most of the catalysts are applied in the production of synthetic gas from glycerol and are composed mainly of carbon and hydrogen oxides, using reagents such as steam and CO_2 (dry). Among these techniques, catalytic steam reforming generally occurs when a significant amount of carbon monoxide reacts with the added steam and undergoes the water vapor displacement reaction that results in the formation of carbon dioxide and hydrogen [42], while glycerol dry reforming (GDR) offers a better way to produce H_2 as it uses greenhouse gas (CO_2) as a raw material. Furthermore, this reaction can be conducted at atmospheric pressure while producing a high yield of H_2 [43,44].

To increase hydrogen production by steam catalytic reforming, the choice of appropriate catalysts is crucial. According to the literature, ruthenium (Ru), rhodium (Rh), platinum (Pt), nickel (Ni), and cobalt (Co) have shown catalytic activity on catalytic steam reforming. Among them, catalysts with Ni supported on different inorganic oxides and their mixtures (such as Al_2O_3, MgO, CeO_2, ZrO_2, TiO_2, and SiO_2) are the most investigated due to their low cost and high availability [2,7,45]. However, although Ni is effective in cleaving $-CH_3$, $-CH_2-$, $O-H$, and $C-C$ bonds, its activity in the water–gas displacement reaction is limited, in addition to its vulnerability to sintering and coke training [2].

Following this trend, an interesting approach was adopted by Sahraei et al. [46] which produced three integrated works. First, they investigated the potential of slag oxide metallurgical residues containing titanium oxides ($FeTiO_3$–Fe_2O_3) by solid state impregnation (SSI) as a catalyst (Ni-UGS) in catalytic steam reforming for the production of hydrogen, obtaining a Gly conversion of 87% with an H_2 yield of 79%. The catalytic performance of Ni-UGS was superior to a commercial alumina-based steam reforming catalyst with higher Ni content (29.8% by weight): 86% conversion of Gly gas with 71% H_2 yield. Better results were obtained in a second work by the same group [47], making a comparative study of Ni-UGSO catalysts prepared by ultrasound-assisted SSI and WI methods with Ni loading (5%), providing almost complete conversion of Gly into gaseous products with high H_2 yield (80.7%). According to the authors, the good performance of the SSI-5%Ni-UGSO catalyst, and the synergistic effect observed between Ni and Fe/Mg by the formation of active sites Ni-Fe_2O_4 and Ni-MgO through the method of state synthesis, benefited both Gly conversion and H_2 selectivity.

Recently, the same group [45] published the third comparative study on the performance of M-UGSO catalysts promoted by M (1% Rh and 1% Ru), presenting better performance in the conversion of Gly (94% in gaseous products with a yield of 74% in H_2), comparable to 1% Rh-UGSO (100% and 78%, respectively), and surpassing 1%Ru-UGSO (94% and 71%, respectively) as catalysts based on noble and expensive metals. Desgagnés and Iliuta [48] studied the kinetics and mechanism of the catalytic steam reforming process, employing an innovative and environmentally friendly 5%Ni-UGSO [47].

In another study, Aissaoui et al. [49] developed a stabilized sorbent–catalyst hybrid material (CaO-UGSO10/NiO) with 10% by weight of UGSO and 20% of NiO that was applied in the steam reforming process of Gly. The results of the operation showed production of H_2 with high purity and yields (95% and 93%, respectively).

On the other hand, Roslan et al. [44] evaluated the performance of an Ni-based catalyst supported on γ-Al_2O_3 that was prepared from aluminum slag (AD) before use as a catalyst support. The extracted γ-Al_2O_3 (EGA3) was produced from the acid leaching of the aluminum slag with the ammonia precipitation technique at a calcination temperature of 800 °C. It showed the best purity (100%) with a surface area of 267.5 m^2 g^{-1}, after which it was impregnated with 15% Ni by the ultrasound method before the evaluation in the reforming dry glycerol reaction (GDR). Studies on the catalytic activities of the

reforming dry glycerol (GDR) reaction revealed that 15% Ni/EGA3 reached maximum catalytic activity with 56.7% conversion of Gly and 44.7% of H_2 at 800 °C.

Subsequently, Okoye et al. [50] used modified ladle furnace (LF) steel slag residues (calcined at 800 °C) with various sodium hydroxide (NaOH) fillers to increase the stability and basic strength of the material. The LF were incorporated with 10% NaOH by mass and promoted 99% Gly conversion. The reduction in the performance of NaOH-LF can be partially attributed to the leached constituents of the materials and the adhesion of organic matter in the pores of the catalyst.

Gonçalves et al. [51] proposed to transform several industrial residues which proved to be efficient catalysts for the etherification of Gly. Different industrial residues can be used as catalysts and catalytic supports and applied in different reactions for the conversion and valorization of glycerol.

2.5. Red Mud

Das and Mohanty [52] reported the use of red mud residue (RM) from the calcined aluminum industry at different temperatures between 400 °C and 800 °C and applied as a catalyst, without chemical pretreatment or incorporation of any other active components, for the efficient production of glycerol carbonate through the transesterification of glycerol with dimethyl carbonate. RM calcined at 500 °C (RM-500) had the maximum concentration of active sites of $NaAlO_2$ and Ca_2SiO_4, thus producing the highest catalytic activity (92.02% GC yield) achieved at a reaction temperature of 75 °C and a 90 min reaction time. The RM-500 catalyst showed excellent resistance, with only a 4.2% reduction in glycerol carbonate yields, to Gly transesterification in the presence of initial impurities such as water and methanol in the initial reaction mixture. The kinetic study suggested a pseudo-first-order reaction for transesterification of Gly in the RM-500 catalyst with a rate constant K of $0.1364 \ s^{-1}$ at 75 °C. RM-500 showed lower stability when reused for the second time, and activity continued to decrease until the fourth reuse due to leaching of some active components.

In another study [53], the catalyst (RM-30%-800), prepared with a load of 30% K in RM and calcined at 800 °C, produced the highest activity and stability in relation to RM-500, with 78.9% Gly conversion even after four reuse cycles.

2.6. Activated Carbon

Glycerol, one of the 12 main chemical building blocks, can be transformed by the deoxygenation process (Figure 5). The work of Zacharopoulou et al. [20] evaluated Mo-based catalysts supported on charcoal, and the catalyst (Mo/BC) proved to be an efficient catalyst for catalytic hydrodeoxygenation of glycerin aimed at the selective production of propylene with 100% selectivity in the gas phase under typical reaction conditions. Specifically, the Mo $^{4+}$ and Mo $^{5+}$ species catalyze and selectively cleave the CO bond and generate a C=C bond, resulting in the complete removal of oxygen from the Gly molecule through a reverse Mars–van Krevelen mechanism. The catalytic results validate that propylene can be produced via hydrodeoxygenation of Gly.
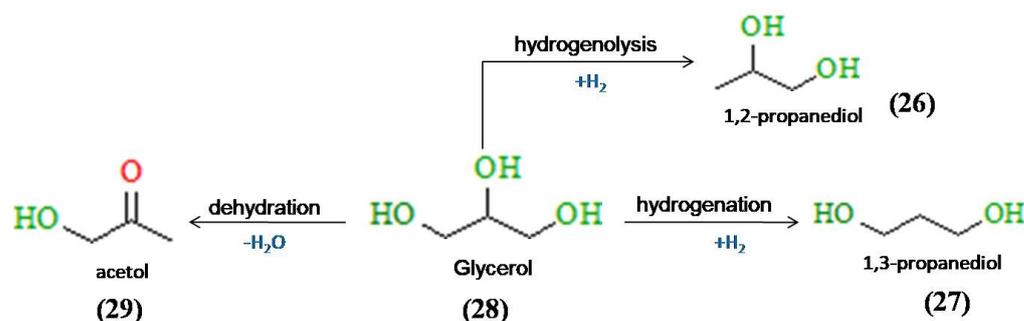

Figure 5. Reactions of the deoxygenation process.

In another study by Gallegos-Suarez [15], an aqueous glycerol solution of several catalysts based on ruthenium supported on activated carbon, high surface area graphite, multiwalled carbon nanotubes, and KL-zeolite, respectively, were investigated in the reported protocol (all samples were produced under the same conditions). However, the least active catalyst, with low conversion to glycerol (Gly, 11.0%), was highly selective for ethylene glycol (EG, 63%) and moderately selective for 1,2-propanediol (1,2-PDO, 14%). The EG can be attributed to the very low ratio of acid sites/metal sites.

The studies by Zacharopoulou et al. [20] and Gallegos-Suarez [15] showed that activated charcoal proved to be an efficient alternative in the application of heterogeneous catalysis in the conversion of glycerol.

In view of the 12 principles of green chemistry, carbon catalysts have recently emerged as promising solid acid catalyst for acid catalysis. In this context, glycerol esterification was investigated by Sánchez et al. [54] using a carbon-based catalyst prepared by sulfonation of carbonized sucrose (3 h at 673 K), which showed approximately 99% conversion and high selectivity to triacetyl glyceride (50%), while esterification under the same conditions using a conventional catalyst such as Amberlyst-15 also gave over 99% conversion, but with a triacetyl glyceride selectivity of around 10%. Therefore, these materials can be an alternative to other commercial heterogeneous acid catalysts such as commercial acid exchange resins. Active carbons can come from different sources, and lignocellulosic biomass residues have been studied as sources for these catalysts.

2.7. Lignocellulosic Biomass

Lignocellulosic biomass is one of humanity's first energy sources, since wood, for example, has been used as a combustion fuel for centuries, and activated carbons obtained from lignocellulosic residues are efficient as catalysts [55]. Most of the catalytic supports studied here have characteristics that allow impregnation with acidic and basic elements. For catalysts applied in the transesterification reaction of glycerol, the basic character is widely used and the reduction of basic groups reduces the catalytic efficiency, as in the recent and pioneering study by Wang et al. [56], who used calcined corn cob residues (CCR-500) that show relatively high basicity (8.8 mmol g^{-1}) and satisfactory catalytic activity with a Gly conversion of 98.1% and a GC yield of 94.1%. The result of the reuse experiment indicated that the catalytic activity of CCR-500 gradually decreased the Gly conversion and GC yield, from 98.1% and 94.1% to 78.2% and 74.8%, respectively, after the fourth reuse, the K content decreased simultaneously from 10.8% to 6.1%, and the Cl content decreased from 3.4% to 0%.

In another study, Okoye et al. [6] used empty palm fruit bunches (EFB) calcined at different temperatures (300–600 °C) as a catalyst for the synthesis of GC in an autoclave reactor. Increasing the calcination temperature propagated the crystalline phase transition from $KAlSiO_4$ to $K_2Mg(SiO_4)$, incorporating more K^+ into the tetrahedral structure of the SiO_2 connected with $Mg^{2+}O_4$, which improved the basicity to reach 95.7% GC yield, under 5% by weight catalyst concentration, 90 °C, and an initial 3:1 DMC/Gly molar ratio in 45 min reaction. The catalyst maintained 85.2% GC yield after four reuses.

Other published works show that acid catalysts are also efficient in glycerol conversion. In the studies by Gonçalves et al. [18] and Domínguez-Barroso et al. [57], the biomasses were modified to introduce acidic surface sites by treatment with H_2SO_4. The functionalized materials achieved high glycerol conversion.

Goncalves et al. [18] studied the preparation of acid carbon-based catalysts called GC-X, where X is the glycerin:acid (mglycerin:mH$_2$SO$_4$) mass ratio used: 3:1, 2:1, 1:1, 1:2, and 1:3 of the biodiesel residue. The coals obtained in 1:2 and 1:3 ratios showed high total acidity (3.8 mmol g^{-1}), reaching about 84% of Gly conversion and about 95% of selectivity to solketal. Furthermore, the surface groups (–SO$_3$H) of the carbon-based catalysts showed high stability and good recycling capacity after different reactions under the conditions tested in this study.

Domínguez-Barroso et al. [57] established a methodological procedure to obtain the cellulose-based catalyst (SO_3HC) through different steps of pyrolysis (400–800 °C), chemical activation with nitric acid (HNO_3), and acid functionalization (SO_3HC). The catalyst presented high surface area (25 m^2 g^{-1}) and an acid site density of 2.9 mmol·H$^+$ g^{-1}, and presented a high performance, with complete glycerol conversion and reaching 99% selectivity of solketal.

Recently, Malaika et al. [58] reported that carbon preparation via partial carbonization of biomass-based substrates with H_2SO_4 proved to be a simple, low-cost, and environmentally friendly synthesis approach, allowing for a high conversion of glycerol (above 95%), and z satisfactory combination of the selectivity of diacetyl glyceride and triacetyl glyceride (above 70%) was obtained within 2 h, demonstrating very good stability in four subsequent reaction cycles. The concentration of –SO_3H groups proved to be crucial for the efficient production of higher esters, and a relationship between the activity of carbon samples and the concentration of sulfonic acid groups was observed.

Tao et al. [17] used the residual biomass of willow catkins as a raw material to prepare sulfonated carbon catalysts (Scheme 1). The catalyst led to a higher glycerol conversion (98.4%) and selectivity for monoacetyl glyceride (32.8%), diacetyl glyceride (54.5%), and triacetyl glyceride (12.7%), respectively, showing that a higher-strength acid increased the glycerol conversion, and the total yields in diacetyl glyceride and triacetyl glyceride increased significantly. The sulfonated carbon catalysts remained efficient after six cycles during the regeneration step due to the lower loss of the –SO_3H group by hydrolysis during the reactions.
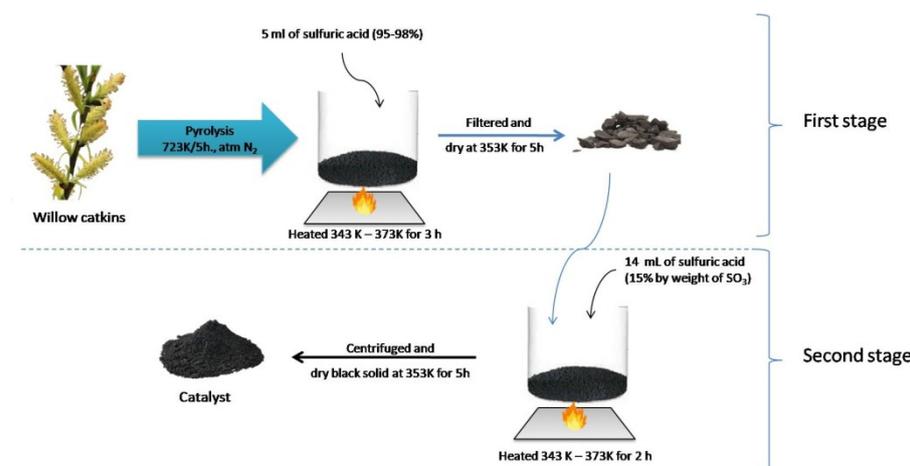
Scheme 1. Preparation of a catalyst based on willow catkins.

In 2021, a new study developed by Nda-Umar and collaborators [19] demonstrated the performance of carbon derived from PKS (Palm Kernel Shell) functionalized with ethane sulfonic acid and applied as a catalyst (ESA) in the acetylation of Gly. The response surface methodology (RSM) was used to optimize the process, and the catalyst showed better performance with mean values of 99.03 ± 0.14% for glycerol and 6.91 ± 0.56, 54.86 ± 0.42, and 37.73 ± 0.21% selectivity for monoacetyl glyceride, diacetyl glyceride, and triacetyl glyceride, respectively. In the reuse test, the catalyst showed excellent performance in the conversion of glycerol (99%) and in the selectivity of diacetyl glyceride (58.2%) for the five reaction cycles.

Considering these premises, two ecologically correct alternatives were identified: the conversion of glycerol, a by-product of biodiesel, into value-added products through suitable catalysts produced from agro-industrial residues. Sulfonated carbon catalysts prepared from agro-industrial residues, bagasse sugarcane (CAA), coconut husk (CHC), and coffee grounds (CGC) were reported by Gonçalves et al. [16]. These catalysts proved to be efficient for the etherification of glycerol with tert-butyl alcohol (TBA) reaching equilibrium after 4 h of reaction, with a glycerol conversion of 81.8%, 61.5%, and 61.5% to

SCC-S, CHC-S, and CGC-S, respectively. Changmai and colleagues [59] investigated the synthesis of a highly basic catalyst based on ash from the bark of Musa accuminata. Applied in the transesterification of Gly with dimethyl carbonate using microwave irradiation, its results indicated that the reaction conversion was 99% glycerol and there was a higher selectivity (99.5%) for glycerol carbonate.

Other agro-industrial residues were sulfonated. Zhao et al. [22] selected peanut husk biomass from agricultural by-products as starting material to prepare a sulfonated carbon catalyst, and the peanut husk was partially carbonized. This treatment proved to be an efficient and environmentally benign catalyst for the complete conversion of Gly in the etherification reaction and a selectivity of 92.1%. Furthermore, the activity of sulfonated peanut husk catalysts remained almost unchanged even after five cycles. Due to its low cost and easy availability, this catalyst has good application prospects.

Galhardo et al. [60] carried out a comparative study between sulfonated carbons prepared from carbonized rice husks and subsequently treated with H_2SO_4. Their results showed better catalytic performance in the esterification and etherification of Gly with acetic acid and tert-butyl alcohol, respectively. In the Gly esterification reaction, 90% conversion was observed after 5 h of reaction, with selectivities of 11%, 52%, and 37% for MAG, DAG, and TAG, respectively. In the etherification, a conversion of 53% was obtained, with a selectivity of 25% for DTBG and TTBG. Thus, the use of sulfonated carbons in the conversion of Gly showed a promising perspective for adding value to the rice and biodiesel production chains using their by-products: rice husk and glycerol.

2.8. Glycerol

Glycerol is an industrial waste that can be transformed into value-added products. Etherification of glycerol can be carried out with various sources of alcohol, for example, tert-butyl alcohol. The reaction products can be used as oxygenated additives for fuels such as diesel and biodiesel, leading to an environmentally and economically attractive production cycle. Studies reported in the literature indicate that the high acidity and porous structure of the catalysts favor the reaction [21,36].

Seeking to reduce preparation costs with carbonization time, Mantovani et al. [61] also studied the preparation of carbon with high acidity (39 mmol H^+ g^{-1}) from biodiesel residue (glycerin) carbonized in the presence of H_2SO_4 in the proportion of 1:3 m/m in a closed autoclave at 180 °C for 1 h. A high yield of about 43% was achieved for MTBG and 20% for DTBG+TTBG, respectively. In addition, the excellent reuse of the catalyst with constant activity in the five reactions evaluated was also confirmed.

Esterification, in Figure 6, of glycerol (30) to acetins is quite attractive due to versatile industrial applications ranging from cosmetics to end-product fuel additives including monoacetyl glyceride (MAG) (31), diacetyl glyceride (DAG) (32), and triacetyl glyceride (TAG) (33). A special interest has been focused on diacetyl glyceride and triacetyl glyceride because of their potential to be used in large quantities as valuable additives for biodiesel and petrofuels.

A study developed by Chandrakala et al. [23] demonstrated the excellent activity of the glycerol-based solid acid catalyst (concentrated Gly and H_2SO_4 treated at 220 °C for 20 min) for the preparation of triacetyl glyceride in a two-step method with lower molar ratios of acetic acid and acetic anhydride in shorter reaction times. To obtain 100% glycerol conversion, use 22, 67, and 11% MAG, DAG, and TAG, respectively, followed by acetylation with one mole of acetic anhydride for 30 min using 5% by weight of Gly-derived catalyst to obtain 100% of TAG. The recovered catalyst maintained its performance without significant losses in its initial activity for five consecutive cycles.
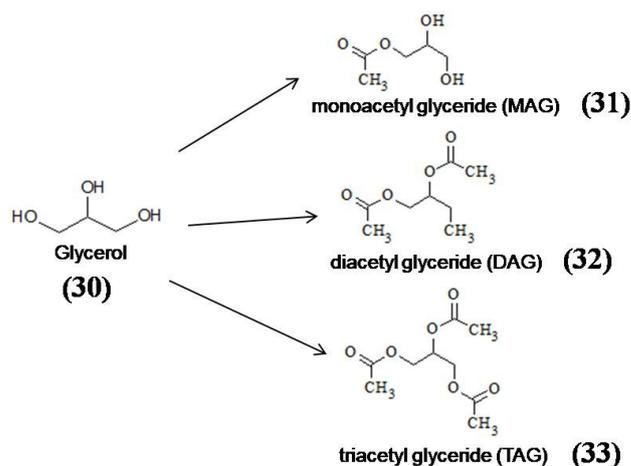
Figure 6. Esterification of glycerol into satins.

3. Conclusions and Perspectives

Compared to homogeneous catalysts, heterogeneous catalysts can provide promising greener routes, mainly using low-cost waste and materials for a future sustainable economy.

Within the biorefinery concept, glycerol is an important molecule to be used as a raw material for a wide variety of value-added chemical products, and several heterogeneous acids and basic catalysts with lower preparation costs have been used in different reaction processes, such as hydrogenolysis, etherification, esterification, acetalization, and ketalization, among others. The great availability and versatility of glycerol, with the presence of its hydroxyl groups, allow for the conversion of this residue into different products and even its use as a raw material for the production of new catalysts.

The depth of literature reported in this review underlines the feasibility and virtuosity of this approach in the field of sustainable biomass conversion. By deriving both the raw material and the catalyst from waste, the Circular Economy principle is applied to its fullest scale, paving the way for waste-free industrial applications. In addition, it should be noted that there is still ample room for progress on this topic. Some examples are the investigation of new catalysts prepared from waste materials considering even more diversified mineral and lignocellulosic residues or the reduction of production costs for the recovery of glycerol. Finally, great prospects arise considering the involvement of more advanced techniques related to nanomaterials, such as single-atom catalysis and 3D printing technologies, which can improve performances and increase the scope for broader and higher value-added chemistry.

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